

## Synthesis and molecular structures of dialkylselenonium methylide complexes of indium tribromide

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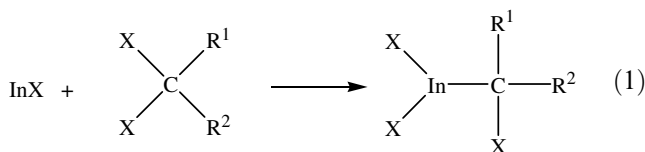
### Abstract

The reaction of bromomethyl-dibromo-indium(III), Br<sub>2</sub>InCH<sub>2</sub>Br with dialkylselenides, R<sup>1</sup>SeR<sup>2</sup> (R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; R<sup>1</sup> = R<sup>2</sup> = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) afforded the corresponding dialkylselenonium methylide complexes of indium tribromide, Br<sub>3</sub>InCH<sub>2</sub>SeR<sup>1</sup>R<sup>2</sup>, which were fully characterized by NMR spectroscopy and single crystal X-ray diffraction studies. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Indium; Organoindium; Carbenoid; Ylid; Zwitterion; Crystal structure

### 1. Introduction

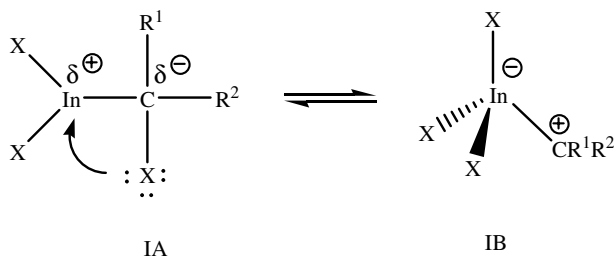
The oxidative insertion of indium monohalides, InX, into a carbon–halogen bond of *gem*-dialkyldihalides, R<sup>1</sup>R<sup>2</sup>CX<sub>2</sub> produces the  $\alpha$ -halogenoalkyl-indium(III) compounds of general formula X<sub>2</sub>InCR<sup>1</sup>R<sup>2</sup>X (Eq. (1)) [1]. It is possible to modulate the electronic character of the  $\alpha$ -halogenoalkyl substituent by the correct choice of the R<sup>1</sup> and R<sup>2</sup> substituents on the parent dialkyldihalide.



Organoindium compounds containing nucleophilic  $\alpha$ -halogenoalkyl substituents were obtained from *gem*-dihalides containing electron withdrawing groups R<sup>1</sup> and R<sup>2</sup> (X = Br, R<sup>1</sup> = CN, R<sup>2</sup> = H [2]; X = Cl, R<sup>1</sup> = CN, R<sup>2</sup> = Cl [3]; X = Cl, R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>CO, R<sup>2</sup> = H [4]; X = Cl, Br, I, R<sup>1</sup> = Cl, Br, I, R<sup>2</sup> = H [5]), while the carbenoids (I) derived from methylene dihalides, X<sub>2</sub>InCH<sub>2</sub>X (X = Br, I), contain halomethyl substituents of considerable electrophilic character, resulting in a strong interaction of the  $\alpha$ -halogen atom with an empty metal orbital. This analysis allows an interpretation of the reactivity of the X<sub>2</sub>InCH<sub>2</sub>X molecules in terms of the tautomeric relationship shown in Scheme 1 [6].

The addition of a soft neutral ligand L to the X<sub>2</sub>InCH<sub>2</sub>X molecules yields the corresponding X<sub>3</sub>InCH<sub>2</sub>L adduct, in which the ligand L is directly attached to the methylene carbon. This paper reports on an extension of these studies. We have now prepared new selenonium methylide complexes of indium tribromide, which were fully characterized by NMR and X-ray diffraction studies.

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Scheme 1.

## 2. Experimental

### 2.1. General

Indium monobromide was prepared by heating indium metal and indium tribromide in a vacuum sealed tube at 450 °C. Methylene bromide (Aldrich) was dried over Linde 4 Å molecular sieves.  $\text{Br}_2\text{In}(\text{diox})_2\text{CH}_2\text{Br}$  was prepared from  $\text{InBr}$  and  $\text{CH}_2\text{Br}_2$  as described earlier [6]. 1,4-Dioxane (diox) was dried over sodium and benzophenone, and distilled just before use from the blue ketyl form. Chloroform (ACS grade) was used as supplied. All preparative work was carried out under dry nitrogen atmosphere, up to the isolation of final products. Proton, carbon and selenium (diphenyl diselenide as internal standard) NMR spectra were recorded on the Bruker DPX-200 and DPX-400 instruments.

### 2.2. Preparation of dialkylselenides, $\text{R}^1\text{SeR}^2$ , **2** (**a** = $\text{R}^1 = \text{CH}_3$ , $\text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ ; **b** = $\text{R}^1 = \text{C}_2\text{H}_5$ , $\text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ ; **c** = $\text{R}^1 = \text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ )

The dialkylselenide ligands were all prepared from dibenzyl diselenide, which was made from  $\text{NaBH}_4$ , elemental selenium and benzyl chloride, according to the literature [7]. Thus, 510 mg (1.50 mmol) of dibenzyl diselenide was suspended in ethanol (20 mL) in a round bottom flask.  $\text{NaBH}_4$  (3 mmol) was added as a solid to the suspension and the reaction kept under magnetic stirring until a clear solution was obtained. At this point, 3 mmol of the corresponding alkyl halide  $\text{R}^1\text{X}$  (**a** =  $\text{R}^1 = \text{CH}_3$ ,  $\text{X} = \text{I}$ ; **b** =  $\text{R}^1 = \text{C}_2\text{H}_5$ ,  $\text{X} = \text{Br}$ ; **c** =  $\text{R}^1 = \text{C}_6\text{H}_5\text{CH}_2$ ,  $\text{X} = \text{Cl}$ ) was added via syringe and the mixture stirred for additional 4 h. After this period, the reaction was quenched with water, the organics extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 20$  mL). The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ), evaporated to dryness to give an oil, which was purified by column chromatography over silical gel with hexane. This procedure gives **2a–c** in the following yields (**a** = 82%, **b** = 67%, **c** = 69%). Compounds **2a–c** were characterized by  $^1\text{H}$  NMR spectroscopy:

Benzyl-methyl-selenide, **2a** (colorless oil):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.22$  (s, 5H), 3.69 (s, 2H), 1.85 (s, 3H);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 170$  [8].

Benzyl-ethyl-selenide, **2b** (colorless oil):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.22 (s, 5H), 3.73 (s, 2H), 2.44 (q,  $J = 7.5$  Hz, 2 H), 1.31 (t,  $J = 7.5$  Hz, 3H);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 284$ .

Dibenzylselenide, **2c** [yellow solid, mp = 45–46 °C (Lit. [7] 45.5 °C)]:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.18 (m, 5H), 3.75 (s, 2H);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 331$  [8].

### 2.3. Preparation of dialkylselenonium methylide complexes of $\text{InBr}_3$ , $\text{Br}_3\text{InCH}_2\text{SeR}^1\text{R}^2$ , **3** (**a** = $\text{R}^1 = \text{CH}_3$ , $\text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ ; **b** = $\text{R}^1 = \text{C}_2\text{H}_5$ , $\text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ ; **c** = $\text{R}^1 = \text{R}^2 = \text{CH}_2\text{C}_6\text{H}_5$ )

$\text{InBr}$  (195 mg, 1 mmol) was suspended in 1,4-dioxan (8 mL) in a Schlenk flask under dry  $\text{N}_2$  atmosphere. To this solution was added  $\text{CH}_2\text{Br}_2$  (869 mg, 0.35 mL, 5 mmol) and the suspension was stirred until complete dissolution of the red  $\text{InBr}$  solid. A clear colorless solution was obtained. The volatiles were removed from this solution under high vacuum to produce a white solid (the bis-dioxan adduct of  $\text{Br}_2\text{InCH}_2\text{Br}$ ). The solid was re-dissolved in dioxan (8 mL) and to this solution was added the corresponding dialkylselenide **2a–c** (1 mmol). The reaction was kept under stirring for 6 h, after which the volatiles were again removed under high vacuum to produce oily materials, which were dissolved in hot chloroform (15 mL). From the solutions, crystalline  $\text{Br}_3\text{InCH}_2\text{SeR}^1\text{R}^2$  compounds precipitate upon cooling to room temperature. The crystals were filtered and dried under vacuum (Yield: **3a** = 40%, **3b** = 70%, **3c** = 75%). The  $\text{Br}_3\text{InCH}_2\text{SeR}^1\text{R}^2$  compounds were characterized by NMR spectroscopy and single crystal X-ray diffraction studies.

Benzyl-methyl-selenonium-methylide-tribromo-indate(III) (**3a**), (mp = 113–115 °C):  $^1\text{H}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 7.47$ –7.59 (m, 5H), 4.86 (d,  $^2J = 11.7$  Hz, 1H), 4.78 (d,  $^2J = 11.7$  Hz, 1H), 2.78 (s, 3H), 2.47 (d,  $^2J = 10.6$  Hz, 1H), 2.38 (d,  $^2J = 10.6$  Hz, 1H);  $^{13}\text{C}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 132.66$ , 131.48, 131.31, 131.21, 47.29, 22.36; (DEPT = 135): 132.66 ( $\text{C}_{\text{ar}}\text{-H}$ ), 131.48 ( $\text{C}_{\text{ar}}\text{-H}$ ), 131.21 ( $\text{C}_{\text{ar}}\text{-H}$ ), 47.29 ( $\text{CH}_2$ ), 22.36 ( $\text{CH}_3$ );  $^{77}\text{Se}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 370$ .

Benzyl-ethyl-selenonium-methylide-tribromo-indate(III) (**3b**), (mp = 131–132.5 °C):  $^1\text{H}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 7.46$ –7.64 (m, 5H), 4.86 (d,  $^2J = 11.8$  Hz, 1H), 4.79 (d,  $^2J = 11.8$  Hz, 1H), 3.37 (m, 2H), 2.47 (s, 2H), 1.54 (t,  $J = 7.50$  Hz, 3H);  $^{13}\text{C}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 132.44$ , 131.72, 131.42, 131.30, 45.60, 36.26, 21.93, 11.32; (DEPT = 135): 132.44 ( $\text{C}_{\text{ar}}\text{-H}$ ), 131.42 ( $\text{C}_{\text{ar}}\text{-H}$ ), 131.30 ( $\text{C}_{\text{ar}}\text{-H}$ ), 45.60 ( $\text{CH}_2$ ), 36.26 ( $\text{CH}_2$ ), 11.32 ( $\text{CH}_3$ );  $^{77}\text{Se}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta = 415$ .

Dibenzyl-selenonium-methylide-tribromo-indate(III) (**3c**), (mp = 152–154 °C):  $^1\text{H}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:

$\delta = 7.42\text{--}7.55$  (m, 10H), 4.80 (d,  $^2J = 11.7$  Hz, 2H), 4.73 (d,  $^2J = 11.7$  Hz, 2H), 2.39 (s, 2H);  $^{13}\text{C}$  NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta = 132.44$ , 131.49, 131.34, 131.23, 46.33, 22.74; (DEPT = 135): 132.44 (C<sub>ar</sub>-H), 131.34 (C<sub>ar</sub>-H), 131.23 (C<sub>ar</sub>-H), 46.33 (CH<sub>2</sub>);  $^{77}\text{Se}$  NMR ((CD<sub>3</sub>)<sub>2</sub>CO):  $\delta = 432$ .

#### 2.4. Crystallographic studies

Crystals of **3b–c** were mounted in glass capillaries on a STOE IPDSII diffractometer for data collection (see Table 1 for crystal data and structure refinements details). The structure of compound **3b** is disordered; the Se, C(2), C(3) and C(31) atoms adopt two independent positions in the cell with occupancies of 14% and 86%, respectively. The structure was, therefore, refined considering these occupancy factors, with C(31) fixed in U<sub>eq</sub>. (for the structure with 14% of occupancy) and with all hydrogen atoms in idealized positions. The crystal of **3c** proved to be a monoclinic (001) reflection twin. Using the non-overlapping reflections of the stronger exemplar, the structure could be solved by direct methods (SIR2002 [9]). For refinement of the twin model (option HKLF5 in SHELXL-97 [10]), additionally all reflections with good overlap of both exemplars were selected with program TWINXL [11]. Nevertheless, due to many partial overlaps, only 2059 reflections remained available (completeness of 31.6%). The phenyl rings were included as rigid groups (C–C = 1.39 Å, C–C–

C = 120°) in the refinement and for all C atoms isotropic displacement parameters were used. The hydrogen atoms were treated as riding on idealized positions with fixed isotropic displacement parameters taken as 1.2 Å of the corresponding bonding partner. The structure contains two independent molecules (molecules I and II) of similar shape in the asymmetric unit. Other programs used in the crystal structure determination are listed in [12–14].

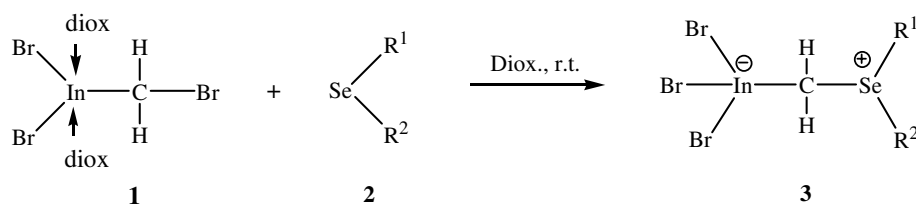
### 3. Results and discussion

Bromomethyl-dibromo-indium(III), **1** prepared from indium monobromide and dibromomethane in 1,4-dioxane (diox.) [6], and the dialkyldiselenides, **2a–c** react to afford the dialkylselenonium methylide-tribromo-indate(III) zwitterions, **3a–c** (Scheme 2). The products were obtained as colorless solids from hot chloroform.

The  $^1\text{H}$  NMR spectra of **3a–c** (see Section 2) show the resonance signal of the methylide group at  $\delta = 2.42 \pm 0.05$  ppm ( $^1\text{H}$ ) and  $\delta = 22.33 \pm 0.04$  ppm ( $^{13}\text{C}$ ). The methylide  $^{13}\text{C}$  resonance is difficult to detect, as the result of the large quadrupole moment of the indium atom ( $I = 9/2$ ); nevertheless we were able to detect it, except for **3a**, after a large number of scans and using a large line broadening parameter ( $LB = 20$ ). Compounds **3a–c** contain an asymmetric selenium center. Accordingly, we have detected, in **3a**, magnetically

Table 1  
Crystal data and structural refinement for **3b–c**

Compound	<b>3b</b>	<b>3c</b>
Empirical formula	C <sub>10</sub> H <sub>14</sub> Br <sub>3</sub> InSe	C <sub>15</sub> H <sub>16</sub> Br <sub>3</sub> InSe
Formula weight (g mol <sup>-1</sup> )	567.72	629.79
Temperature (K)	193(1)	153(1)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, C2/c	Monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions		
<i>a</i> (Å), $\alpha$ (°)	21.779(2), 90	11.3687(8), 90
<i>b</i> (Å), $\beta$ (°)	8.6424(9), 107.192(9)	9.3843(4), 92.355(6)
<i>c</i> (Å), $\gamma$ (°)	17.489(2), 90	34.905(2), 90
Volume (Å <sup>3</sup> )	3144.7(6)	3720.8(4)
<i>Z</i> , <i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	8, 2.398	8, 2.249
Absorption coeff. (mm <sup>-1</sup> )	11.413	9.659
Absorption correction	Numerical	Semiempirical <i>T</i> (min/max) = 0.424/0.699
<i>F</i> (000)	2096	2352
Crystal size (mm <sup>3</sup> )	0.18 × 0.06 × 0.06	0.18 × 0.09 × 0.03
$\theta$ Range for data collection (°)	1.96–25.99	2.10–24.72
Limiting indices	$-26 \leq h \leq 26$ , $-10 \leq k \leq 10$ , $-19 \leq l \leq 21$	$-12 \leq h \leq 12$ , $0 \leq k \leq 9$ , $-41 \leq l \leq 41$
Reflections total/unique	7838/3036	10555/4618
Used for twin refinement	–	2059
Completeness to $\theta$ (%)	98.3	31.6
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup> as (0 0 1) reflection twin
Data/restraints/parameters	3036/13/159	2059/0/165
Goodness of fit on <i>F</i> <sup>2</sup>	0.793	0.982
<i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0398, <i>wR</i> <sub>2</sub> = 0.0630	<i>R</i> <sub>1</sub> = 0.0860, <i>wR</i> <sub>2</sub> = 0.2083
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0988, <i>wR</i> <sub>2</sub> = 0.0730	<i>R</i> <sub>1</sub> = 0.1301, <i>wR</i> <sub>2</sub> = 0.2421
Larg. diff. peak/hole (e Å <sup>-3</sup> )	1.288/–0.647	0.793/–0.845

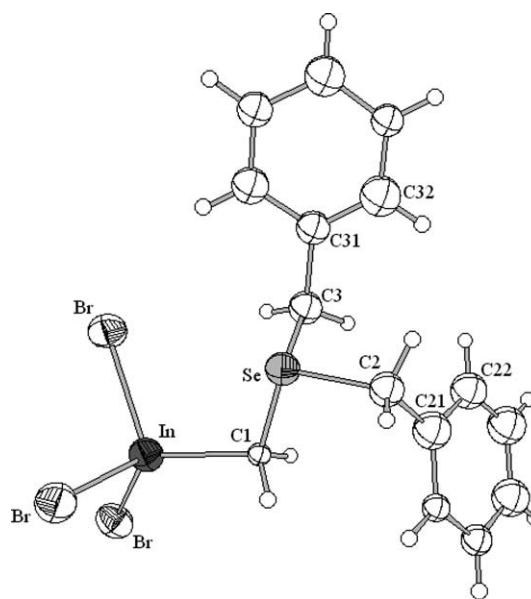
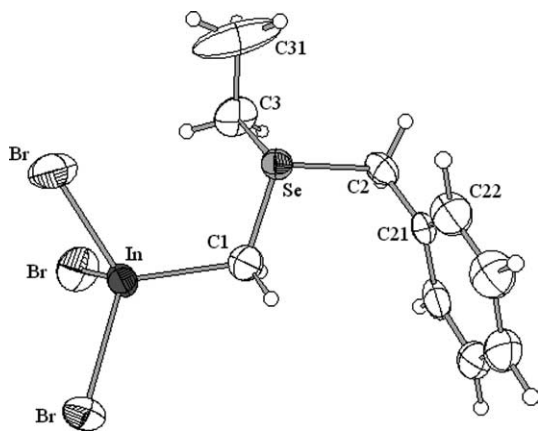


	R <sup>1</sup>	R <sup>2</sup>	Yield (%)
<b>a</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	40
<b>b</b>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Ph	70
<b>c</b>	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	75

Scheme 2.

non-equivalent methylene and benzylic protons that give rise to typical *AB* patterns spectra with  $^2J_{A-B}$  close to 11 Hz. In **3b–c**, only the benzylic protons are magnetically non-equivalent. The  $^{77}\text{Se}$  NMR resonance signals of compounds **3a–c** (see Section 2.3) were detected between 370–432 ppm, in the range (249–538 ppm) reported [8] for other selenium ylids. These signals are considerably deshielded ( $150 \pm 50$  ppm) when compared to the corresponding signals of the parent selenides, **2a–c** (see Section 2.2). The magnitude of this shift is similar to the values (180–250 ppm) normally observed upon alkylation of selenides [8].

The structures of the new selenonium ylids of  $\text{InBr}_3$  **3b–c** were determined by single crystal X-ray diffraction studies. The molecular structure of compound **3b** is depicted in Fig. 1 (molecule with 86% of occupancy). Fig. 2 represents molecule II of compound **3c**. Important bond lengths and angles are summarized in Table 2. The general features of the structures of **3b–c** are in good agreement with those reported for the neutral adducts of ylids of group 15 and 16,  $\text{Br}_3\text{InCH}_2\text{L}$ . The average indium–bromine bond distances of 2.510(1) Å for **3b**, 2.521(6) Å for **3c** (molecule I) and 2.531(6) Å for

Fig. 2. The molecular structure of **3c** with atoms shown as 50% probability ellipsoids.Fig. 1. The molecular structure of **3b** with atoms shown as 50% probability ellipsoids.Table 2  
Important bond lengths (Å) and angles (°) for **3b–c**

	<b>3b</b> <sup>a</sup>	<b>3c</b> (Molecule I)	<b>3c</b> (Molecule II)
In–Br <sup>b</sup>	2.510(1)	2.521(6)	2.531(6)
In–C(1)	2.175(8)	2.13(4)	2.21(3)
Se–C(1)	1.889(9)	1.90(3)	1.86(3)
Se–C(2)	1.958(8)	2.08(4)	1.95(4)
Se–C(3)	1.956(9)	1.97(5)	1.98(4)
C(2)–C(21)	1.48(1)	1.49(4)	1.50(4)
C(3)–C(31)	1.45(2)	1.52(5)	1.55(4)
C <sub>ar</sub> –C <sub>ar</sub>	1.38(2)	1.39 <sup>c</sup>	1.39 <sup>c</sup>
Br–In–Br <sup>b</sup>	111.07(4)	106.4(2)	105.6(2)
Br–In–C(1) <sup>b</sup>	110.0	112(1)	113(1)
C(1)–Se–C(2)	100.8(5)	108(2)	102(2)
C(1)–Se–C(3)	99.4(4)	97(2)	100(2)
In–C(1)–Se	112.8(4)	113(2)	112(1)

<sup>a</sup> Molecule with 86% of occupancy.<sup>b</sup> Mean value.<sup>c</sup> Constraint value.

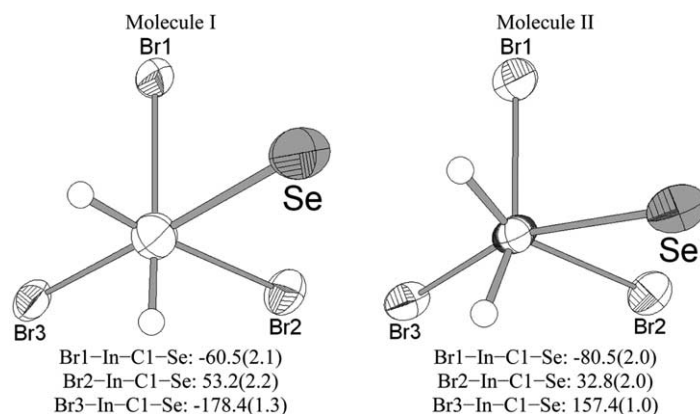


Fig. 3. Selected torsion angles ( $^{\circ}$ ) for **3c** (molecules I and II).

**3c** (molecule II) compare well to those observed in the  $\text{Br}_3\text{InCH}_2\text{L}$  compounds  $\{\text{L} = (\text{C}_2\text{H}_5)_3\text{N}, 2.529(1) \text{ \AA}$  [15];  $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}, 2.512(2) \text{ \AA}$  [16];  $\text{L} = (\text{C}_6\text{H}_5)_3\text{As}, 2.508(6) \text{ \AA}$  [15];  $\text{L} = (\text{C}_6\text{H}_5)_3\text{Sb}, 2.509(5) \text{ \AA}$  [15];  $\text{L} = (\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}, 2.5150(7) \text{ \AA}$  [17]\}. Similarly, the In–C bond distances in **3b** [2.18(1) \AA], **3c** (molecule I) [2.13(4) \AA] and **3c** (molecule II) [2.21(3) \AA] are readily comparable to the values encountered in the cited  $\text{Br}_3\text{InCH}_2\text{L}$  compounds  $\{\text{L} = (\text{C}_2\text{H}_5)_3\text{N}, 2.185(5) \text{ \AA}$ ;  $\text{L} = (\text{C}_6\text{H}_5)_3\text{P}, 2.18(1) \text{ \AA}$ ;  $\text{L} = (\text{C}_6\text{H}_5)_3\text{As}, 2.17(5) \text{ \AA}$ ;  $\text{L} = (\text{C}_6\text{H}_5)_3\text{Sb}, 2.16(3) \text{ \AA}$ ;  $\text{L} = (\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}, 2.189(5) \text{ \AA}\}$ .

The measured bond lengths and angles in molecules I and II of the twinned crystal **3c** are the same within the experimental error. The main difference relating the two structures is in the Br–In–C1–Se torsion angles. Fig. 3 shows the *Newman projections* along the C1–In axis for both molecules with the important torsion angles. In molecule I, a regular staggered conformation is observed, while in molecule II the dibenzylselenide substituent is rotated by  $20^{\circ}$  with respect to the position in molecule I towards an eclipsed conformation.

#### 4. Conclusion

Bromomethyl-dibromo-indium(III) is an organometallic compound containing two electrophilic sites, namely the metal center and the bromomethyl carbon atom. Ligand coordination to the metal is achieved by bromide anion and hard ligands, such as ethers and triphenylphosphine oxide [6]. The soft dialkylselenide ligands,  $\text{R}^1\text{SeR}^2$  coordinate to the soft halomethyl carbon of the carbenoid, forming the dialkylselenium methylide adducts of indium tribromide,  $\text{Br}_3\text{InCH}_2\text{SeR}^1\text{R}^2$ . The new selenium ylides are members of a series of related  $\text{Br}_3\text{InCH}_2\text{L}$  adducts, in which L is a group 15 (N, P, As, Sb) and 16 (S) neutral ligand. As for the related  $\text{Br}_3\text{InCH}_2\text{L}$  compounds, the selenium

ylides are stable compounds and lack reactivity as ylide carriers by thermal rupture of the indium–carbon bond. Other chemical properties, however, still remain completely unexplored, and the study of these properties will be the subject of further research to be reported in due time.

#### 5. Supporting material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC Nos. 254745 (for compound **3b**) and 254746 (for compound **3c**). Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccd.cam.ac.uk>).

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